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Cofacial Assembly of Metallomacrocycles. A Molecular
Engineering Approach to Electrically Conductive Polymers

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This paper discusses a strategy to control molecular stacking interactions in low-dimensional mixed valence materials by locking partially oxidized metallo-macrocycles together in a face-to-face orientation. Thus, doping of the cofacially linked oligomers $[M(Pc)O]_n$ (M = Si, Ge, Sn; Pc = phthalocyaninato) with halogen (I_2, Br_2) or quinone (e.g., TCNQ, DDQ) electron acceptors produces robust, electrically conductive polymers with a wide range of stoichiometries and properties. The new materials have been studied by a variety of physical methods including X-ray diffraction, resonance Raman and infrared spectroscopy,

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ESR, static magnetic susceptibility, and variable-temperature four-probe electrical conductivity. Evidence is presented that some of the polymers have "metal-like" conductivity in the stacking direction and that transport properties within the series can be readily manipulated by rational variation of lattice architecture (e.g., the identity of the metal, M) and acceptor characteristics.

A

COFACIAL ASSEMBLY OF METALLOMACROCYCLES. A MOLECULAR

ENGINEERING APPROACH TO ELECTRICALLY CONDUCTIVE POLYMERS

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INTRODUCTION

In the past few years, the new condensed matter chemistry/-physics interface field of electronic materials having low-dimensional *properties* has undergone dramatic development.[1-6] The preparation of advanced new classes of organic, metal-organic, and inorganic substances with the properties of restricted dimensionality metals has excited theorists and experimentalists alike. This activity is stimulating important breakthroughs in chemical synthetic strategy and methodology, in spectroscopic, structural, and transport analysis, and in the fundamental theoretical descriptions of cooperative phenomena in the solid state. In terms of technology, applications as varied as rectifiers,[7] sensors,[8,9] solar energy conversion elements,[10,11] fuel cell components,[12] switching devices,[13] photoresist elements,[14] chemoselective electrodes,[15,16] electrophotographic devices,[17] and durable synthetic materials to replace metals[17] are being discussed. Speculation on the possibility of high temperature superconductivity remains, as always, a pervasive yet highly speculative motivation.[18,19]

Despite the intense activity in this field, our understanding of the fundamental structural and electronic characteristics which govern charge transport is at an embarrassingly primitive level. This is equally true of the synthetic chemistry presently needed to tailor molecular assemblies for evaluating contemporary theories as well as for optimizing materials performance and processing characteristics. The central focus of our research program has been the development of rational syntheses of new low-dimensional electronic materials and physical studies of the products arising from this effort.[20,21] The goal has been to devise controllable

and systematic chemical approaches to such substances, so that
critical characteristics can be "tuned" and collective properties
correlated with changes in stoichiometry, crystal and electronic
structure, etc. Our initial efforts in this direction involved
materials composed of simple molecular stacks. However, as we
sought greater control over lattice architecture and asked more
fundamental questions about the molecular metallic state, the
structural inadequacies of such materials became readily apparent.

The purpose of this article is to review a new, successful
approach to the control of lattice architecture in low-dimensional
materials. It involves covalently linking and bringing into the
appropriate oxidation state, well-characterized and chemically
flexible molecular subunits. This approach capitalizes upon a
great deal of accumulated knowledge, and offers the possibility of
assembling a wide variety of robust, electrically conductive poly-
mers with well-defined and easily modified primary and secondary
structures.[22-25] We begin with a general discussion of those fac-
tors promoting the molecular metallic state. Next we show how
this information and a cofacial assembly strategy lead to new
types of conductive polymers. Illustrating with the phthalocya-
nine subunit, the chemical and physical properties of the "face-
to-face" polymers are examined as a function of structure and
added dopants.

REQUISITES FOR CONDUCTIVE MOLECULAR MATERIALS

Two general features now appear to be necessary for converting
an unorganized collection of molecules into a conductive molecular
array.[1-6,20,21] First, the component molecules must be positioned
in close spatial proximity, with sufficient intermolecular orbital
overlap to provide a continuous electronic pathway for carrier
delocalization, and in crystallographically similar environments.
With the molecules positioned in this manner, the conduction path-
way has a minimum of energetic "hills" and "valleys." Second, the
arrayed molecules must exist in formal fractional oxidation states
("mixed valence," "incomplete charge transfer," "partial oxidation").
In other words, the molecular entities to be connected in series
must have fractionally occupied electronic valence shells. Within
the framework of a simple one-dimensional Hubbard model, this pre-
requisite reflects the relatively narrow bandwidths $(4t)$ and large
on-site coulomb repulsions (U) in such systems.[1-6] A simplified
valence bond picture of this situation is illustrated in Figure 1;
partial oxidation facilitates charge mobility by creating numerous
electronic vacancies. An analogous decription can likewise be
generated for partial reduction.

Our initial, first-generation strategy for the synthesis of
mixed valent low-dimensional materials involved the cocrystalliza-
tion of planar, conjugated metallomacrocyclic donor molecules (D)

Unoxidized	Partially Oxidized
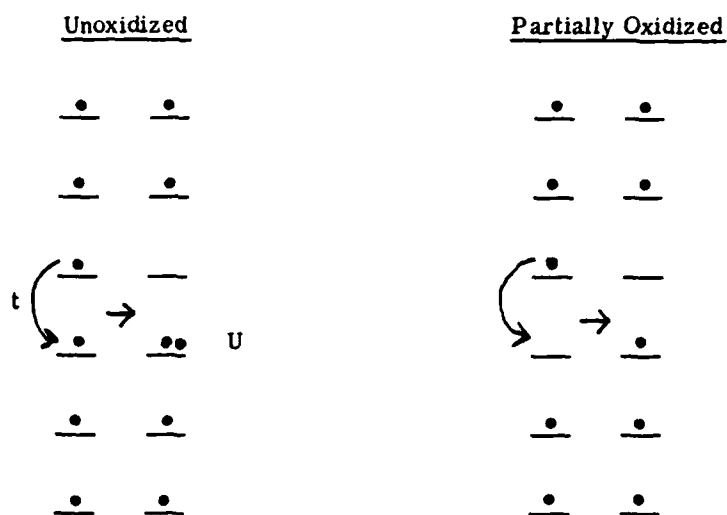
U = electron correlation energy

t = transfer integral ≈ bandwidth/4

Fig. 1. Schematic illustration of the effect of partial oxidation on charge mobility in a low-dimensional system composed of molecular stacks.

having an MN_4 ligation sphere, with halogen acceptors (A) as shown below.[20,21] In optimum cases, the result has been lattices composed of segregated, partially oxidized metallomacrocyclic stacks and parallel arrays of halide or polyhalide counterions. An
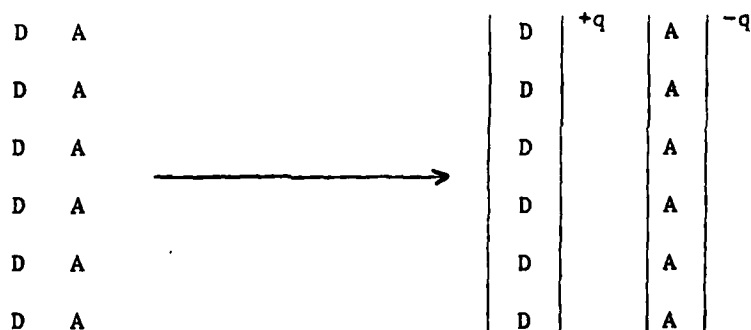
D = donor   A = acceptor

important additional feature of this approach is that the form of the halogen (even if disordered) can be determined in a straight-forward manner by resonance Raman/iodine Mössbauer spectroscopic techniques.[21,26,27] The degree of partial oxidation follows from this information and knowledge of the stoichiometry. This synthetic approach has enjoyed success for metal glyoximates,[28-32] dibenzotetraazaannulenes,[33,34] phthalocyanines,[35-37] and porphyrins.[38] As an illustration, nickel phthalocyanine iodide, $[Ni(Pc)]I_{1.0}$, consists of stacks of staggered $Ni(Pc)^{+0.33}$ units arrayed at 3.244(2) Å intervals and surrounded by parallel chains of I_3^- counterions. The 300°K conductivity of this material in the molecular stacking direction is 300-700 Ω^{-1} cm^{-1} and the temperature dependence is "metal-like" ($\rho \sim T^{1.9}$) down to 60°K.[37] The conductivity is predominantly a ligand-centered phenomenon, and carrier mean free paths are comparable to some of the most conductive "molecular metals."

THE COFACIAL ASSEMBLY STRATEGY

Although the above molecular macrocycle, halogen cocrystallization approach to the synthesis of mixed valent low-dimensional,
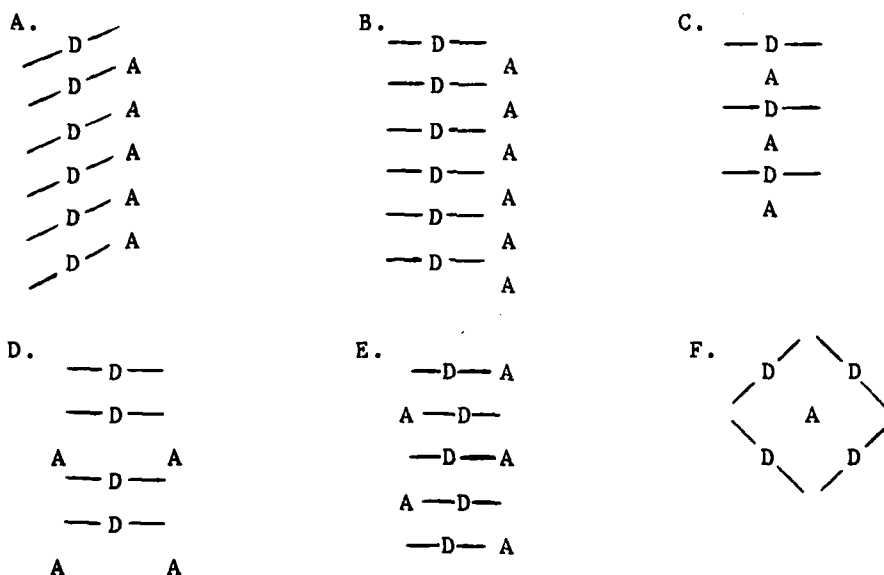

Fig. 2. Schematic illustration of some common structures for donor-acceptor complexes. A. Segregated stacking, canted donors. B. Segregated stacking, D_{nh} donor stacking. C. Integrated stacking. D. Integrated stacking, donor dimers. E. Segregated stacking, zig-zag donor stacking. F. Ion clusters without stacking.

metal-like materials is effective in many cases, it suffers, as do all strategies that rely upon molecular stacking, from a number of weaknesses. For example, in such cases the lattice architecture is dependent upon the unpredictable and largely uncontrollable forces that dictate the stacking pattern, the donor-acceptor orientations, and the stacking repeat distances. Figure 2 illustrates the complexity of the structural problem by depicting some of the types of common donor-acceptor crystallization patterns.[39-44] A frequent pitfall in the design of new materials is that segregated stacks (Figure 2A,B) do not form and that the effort expended in donor or acceptor design is for naught. For example, our efforts to substitute various oxidizing quinones for halogens in the cocrystallization synthesis have failed because integrated stack (Figure 2C,D) insulators are apparently formed.[45,46]

To achieve far greater control over molecular stacking we have employed the assembly process depicted in eq.(1).[22-25] Cofacial

$$\begin{array}{c} \fbox{M} \\ \\ \fbox{M} \\ \\ \fbox{M} \end{array}$$

(1)
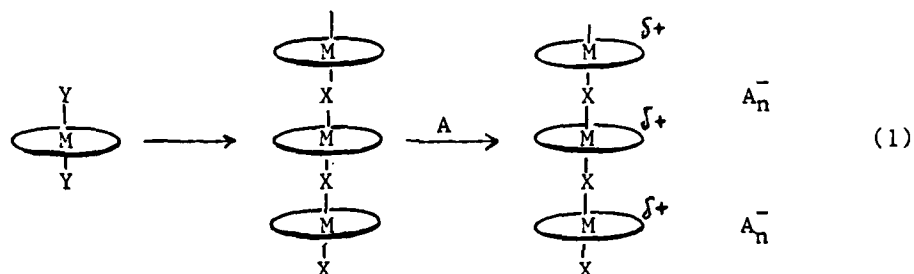
joining is carried out through the formation of strong covalent bonds involving the metallomacrocycle axial substituents (Y). The inherent variability of the metal, macrocycle, and bridging group offers great flexibility in terms of the structures which can be assembled, while the center-to-center mode of joining offers, in contrast to other conceivable modes of linking, superior structural control. Doping can then be carried out using either established halogenation methodology[20,21] or, as a consequence of the enforced stacking, entirely new types of dopants (vide infra).

Our first studies have involved phthalocyanine systems where M = Si, Ge, Sn, and X = O. Thus, $Si(Pc)(OH)_2$, $Ge(Pc)(OH)_2$, and $Sn(Pc)(OH)_2$[47,48] (we have developed an improved synthesis for the Si derivative) can be condensed at $300-400°C/10^{-3}$ torr to form "face-to-face" polymers (Figure 3). Concurrent to doping and transport studies, we have investigated the nature of these materials as polymers. The $[M(Pc)O]_n$ materials have high chemical and thermal stability; moreover, they are not significantly degraded by oxygen or moisture. We find that the polysiloxane polymer can be dissolved in concentrated sulfuric acid and recovered unchanged[49] (typical of phthalocyanines containing non-electropositive metals[50,51]). A rough estimate of the minimum average chain length
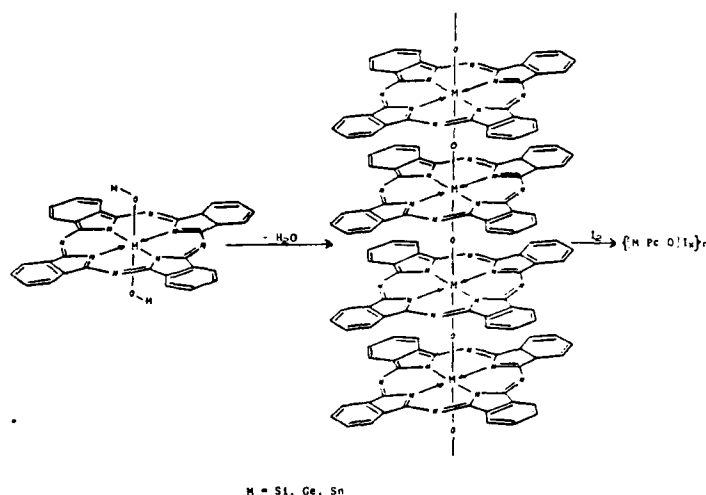
M = Si, Ge, Sn

Fig. 3   Condensation reaction to produce cofacial arrays of Group
         IV metallophthalocyanines.

of $[Si(Pc)O]_n$ produced in the condensation polymerization can be
obtained by Fourier transform infrared spectrophotometric analysis
of the Si-O stretching region. For a typical sample, the degree
of polymerization is estimated to be on the order of ca. 100 sub-
units or more.[52] Prelimiliminary light scattering molecular weight
determinations in sulfuric acid solution are in agreement with
this result.[53]

Structural information on the face-to-face polymers has been
derived from several lines of evidence. We have indexed the X-ray
powder diffraction data in the tetragonal crystal system using
iterative computer techniques.[22-25] Data are very similar to
those from the columnar crystal structures of $[Ni(Pc)]I_{1.0}$[37] and
$Ni(dpg)_2I_{1.0}$.[29] The interplanar spacings in these latter tetrago-
nal structures, determined in single crystal studies, are 3.244(2)
Å and 3.27(1) Å, respectively. The corresponding spacings derived
for the $[M(Pc)O]_n$ materials from the powder diffraction data
depend upon the ionic radius of the Group IV ion and vary from
3.33(2) Å (Si-O-Si), to 3.51(2) Å (Ge-O-Ge), to 3.95(2) Å
(Sn-O-Sn). The reliability of these metrical parameters is
further supported by single crystal diffraction results on the
model trimer $[(CH_3)_3SiO]_2(CH_3)SiO[Si(Pc)O]_3OSi(CH_3)[OSi(CH_3)_3]_2$
which contains three cofacial Si(Pc) units linked by linear
Si-O-Si connections at a distance of 3.324(2) Å.[54] In addition,
the $[Ge(Pc)O]_n$ and $[Sn(Pc)O]_n$ interplanar spacings obtained from
diffraction data are in good agreement with values we estimate
from ionic radii assuming linear Ge-O-Ge and Sn-O-Sn vectors,
i.e., 3.58 Å for $[Ge(Pc)O]_n$ and 3.90 Å for $[Sn(Pc)O]_n$.[22-25]

There is ample precedent for molecules with linear Si-O-Si, Ge-O-Ge, and Sn-O-Sn linkages.[55-58]

HALOGEN DOPING OF COFACIALLY LINKED METALLOPHTHALOCYANINES

Partial oxidation of the $[M(Pc)O]_n$ materials was first carried out using iodination methodology developed in this Laboratory for simple stacked systems. Stirring the powdered polymers with solutions of iodine in aromatic solvents or exposing the powders to iodine vapor results in a substantial iodine uptake. Alternatively, the $[Si(Pc)O]_n$ polymer can be doped by dissolving in sulfuric acid and precipitating with an aqueous I_3^- solution. The stoichiometries which can be obtained depend upon the reaction conditions; representative materials characterized by elemental analysis are compiled in the lefthand column of Table 1. A survey experiment also indicated that a bromine-doped material could be prepared. X-ray powder diffraction studies demonstrate that no major structural change in the face-to-face stack occurs upon halogenation.

Table 1. Physical Data for Polycrystalline Samples of Halogen-Doped $[M(Pc)O]_n$ Polymers

Compound	$\sigma(\Omega^{-1}cm^{-1})300°K$	Activation Energy (eV)	Interplanar Spacing (Å)
$[Si(Pc)O]_n$	3×10^{-8}		3.33(2)
$\{[Si(Pc)O]I_{0.50}\}_n$	2×10^{-2}		
$\{[Si(Pc)O]I_{1.55}\}_n$	1.4	0.04 ± 0.001	3.33(2)
$\{[Si(Pc)O]I_{4.60}\}_n$	1×10^{-2}		
$\{[Si(Pc)O]Br_{1.00}\}_n$	6×10^{-2}		
$[Ge(Pc)O]_n$	$<10^{-8}$		3.51(2)
$\{[Ge(Pc)O]I_{0.31}\}_n$	7×10^{-4}	0.08 ± 0.001	
$\{[Ge(Pc)O]I_{0.62}\}_n$	1×10^{-2}	0.05 ± 0.001	
$\{[Ge(Pc)O]I_{1.94}\}_n$	6×10^{-2}	0.05 ± 0.007	
$\{[Ge(Pc)O]I_{2.0}\}_n$	1×10^{-1}		
$[Sn(Pc)O]_n$	$<10^{-8}$		3.95(2)
$\{[Sn(Pc)O]I_{1.2}\}_n$	1×10^{-6}		3.95(2)
$\{[Sn(Pc)O]I_{5.5}\}_n$	2×10^{-4}	0.68 ± 0.01	
$[Ni(Pc)]I_{1.0}$[a]	7×10^{-1}	0.036 ± 0.001	3.244(2)

[a] Reference 35.

That oxidation of the cofacial array has indeed occurred is con-
firmed by resonance Raman scattering spectroscopy in the poly-
iodide region (Figure 4) which reveals the characteristic totally
symmetric stretching transition of I_3^- ($\nu = 108$ cm^{-1}) and an
accompanying overtone progression. For stoichiometries with I/M
< 3, there are no more than traces of I_5^- ($\nu \approx 160$ cm^{-1}) and no
evidence of free I_2 ($\nu \approx 200$ cm^{-1}).[21] The nature of the doped
$[M(Pc)O^{\delta+}]_n$ electronic structure was also probed by electron spin
resonance (ESR). The symmetry of the lineshapes and the measured
g-values are consistent with π-radical cations, i.e., the unpaired
spin density is in molecular orbitals which are predominantly
ligand in character.[25] A similar conclusion was reached for
$[Ni(Pc)]I_{1.0}$.[37] ESR data for the $\{[M(Pc)O]I_x\}_n$ materials are set
out in Table 2.

$\{[Sn(Pc)O]I_{1.20}\}_n$

$\{[Ge(Pc)O]I_{1.80}\}_n$

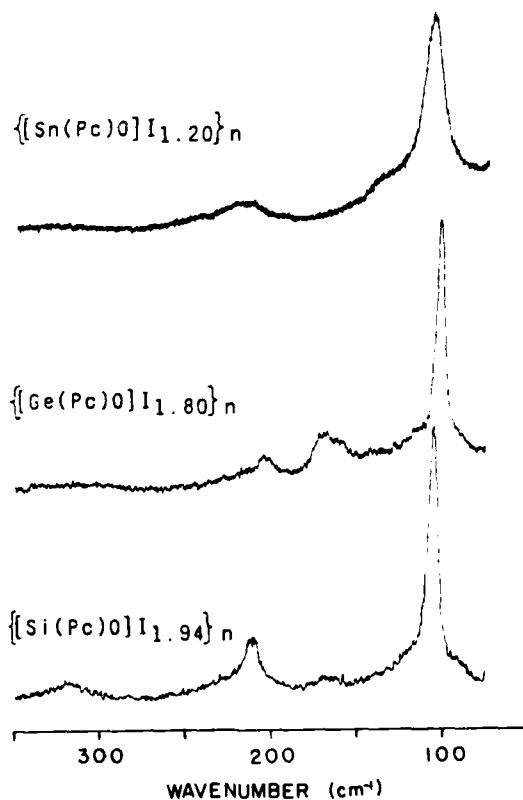$\{[Si(Pc)O]I_{1.94}\}_n$

300   200   100

WAVENUMBER (cm^{-1})

Fig. 4. Resonance Raman spectra ($\nu_0 = 5145$ Å) of iodine-doped
phthalocyanine face-to-face polymers. From ref. 22.

Table 2. Powder ESR Data for Iodinated Phthalocyanine Face-to-Face Polymers

Compound	g(300°K)[a]	Γ(300°K)9G)[b]
{[Si(Pc)O]I$_{1.40}$}$_n$	2.003	5.1
{[Ge(Pc)O]I$_{0.62}$}$_n$	2.002	3.2
{[Sn(Pc)O]I$_{1.20}$}$_n$	2.002	6.0

a
 Average g-value; $g_{\parallel}$ and $g_{\perp}$ are not resolved.
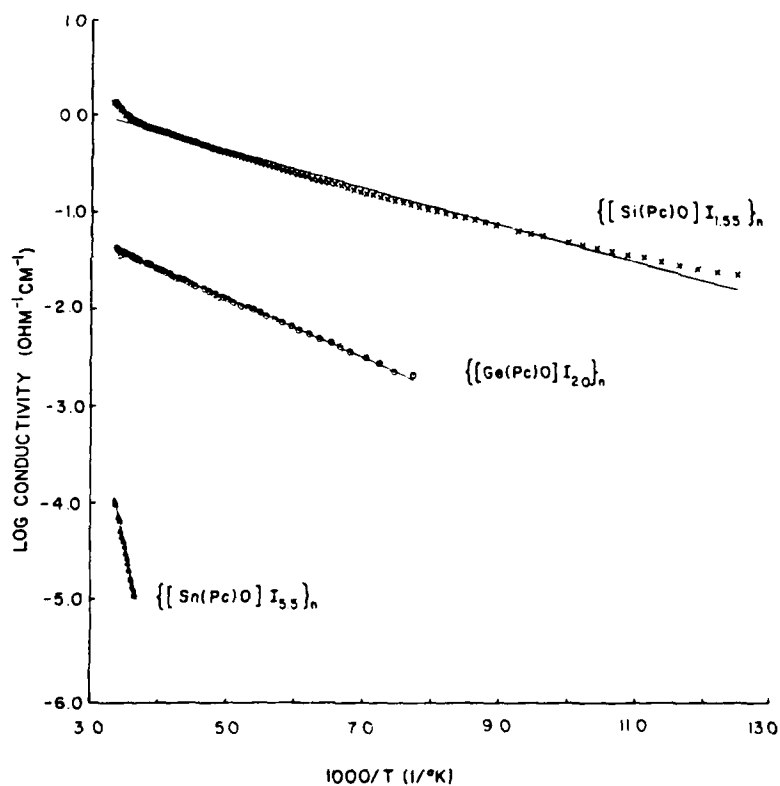b
 Observed linewidth.

Fig. 5. Variable temperature four-probe electrical conductivity data for powders of the iodine-doped, face-to-face phthalocyanine polymers. The straight lines give least-squares fits to eq. (2). From ref. 24.

Four-probe van der Pauw[59,60] electrical conductivity measurements on the $[M(Pc)O]_n$ powders show them to be insulators. However, iodine or bromine doping results in substantial increases in electrical conductivity (Table 1). The general trend in conductivity as a function of metal is $\sigma_{Si} \gtrsim \sigma_{Ge} > \sigma_{Sn}$. Since it is known that the transport characteristics of iodine-oxidized metallophthalocyanines are largely ligand-dominated and relatively insensitive to the identity of the metal,[35-37] the metal dependence of the conductivity observed in the face-to-face polymers is logically ascribed to structural differences such as how the interplanar separation is influenced by metal ionic radius. Indeed, the $\{[Si(Pc)O]I_x\}_n$ interplanar separation is within 0.1 Å of that in the aforementioned "molecular metal" $[Ni(Pc)]_{1.0}$ and the room temperature powder conductivities of the two materials are quite comparable (Table 1). Variable temperature studies indicate that the $\{[M(Pc)O]I_x\}_n$ powder conductivities are thermally activated (Figure 5) and least-squares fits to eq. (2) yield the activation

$$\sigma = \sigma_0 e^{-\Delta/kT} \tag{2}$$

energies shown in Table 1. Powder conductivity measurements are, of course, influenced by interparticle contact resistance and averaging over all crystallographic orientations. Thus, for low-dimensional compounds such as $[Ni(Pc)]I_{1.0}$, powder conductivities are typically 10^2-10^3 less than single crystal conductivities in the stacking direction and exhibit the thermally activated temperature dependencies. Thus, "metal-like" temperature dependence ($d\sigma/dT < 0$) is usually masked. From the powder conductivity data on the $\{[M(Pc)O]I_x\}_n$ materials it is thus reasonable to anticipate that "metal-like" charge transport will be observed in the chain direction for the M = Si and possibly M = Ge materials. Further information on this question is provided by voltage shorted compaction (VSC) techniques[61] which offer a qualitative means to sample stacking axis transport properties in pressed powder samples by deliberately shorting out sources of interparticle resistance. Importantly, the VSC conductivity behavior of $\{[Si(Pc)O]I_x\}_n$ samples is "metal-like."[62] The results of the variable temperature conductivity studies also underscore the robust thermal character of the cofacially arrayed polymers. $\{[Si(Pc)O]I_x\}_n$ samples could be cycled to 300°C with only minor deterioration in room temperature conductivity (apparently due to vaporization of the iodine).

Static magnetic susceptibility measurements by Faraday techniques reveal another characteristic hallmark of "molecular metals" in the $\{[Si(Pc)O]I_x\}_n$ and $\{[Ge(Pc)O]I_x\}_n$ materials. Susceptibilities are only weakly paramagnetic (χ_M = 300-500 x 10^{-6} emu after diamagnetic corrections are made) and are only

modestly dependent on temperature down to $77°K$[22,23]. Studies at
lower temperature are presently in progress.

THE EFFECTIVENESS OF NONHALOGEN DOPANTS

The availability of a low-dimensional system in which the
stacking variable is held constant offers an unusual opportunity,
vis-à-vis those factors stabilizing the mixed valent state,[63-66]
to investigate the effects of dopants which yield integrated stack
structures on reaction with molecular M(Pc) compounds. Thus, it
was of interest to learn whether non-halogen oxidants with redox
potentials similar to halogens could ever produce a partially oxi-
dized, conductive metallophthalocyanine stack. This would help to
define whether the marked efficacy of halogen dopants in forming
mixed valent metallomacrocycles reflects, in addition to redox
potential, a unique structure-forming role (small yet variable
size) or whether other factors (e.g., specific Madelung, exchange,
polarization, van der Waals, or core repulsion terms) might be
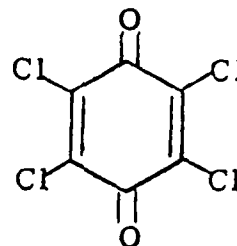important.

Oxidizing quinones such as those shown below form conductive,
mixed valent compounds with a variety of organic donors,[1-5] but
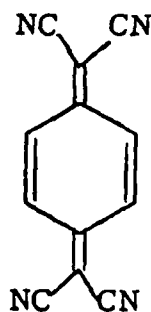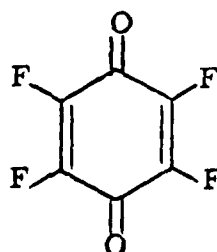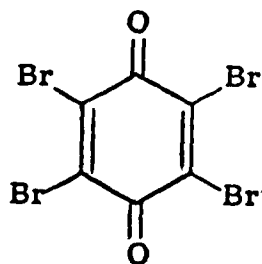
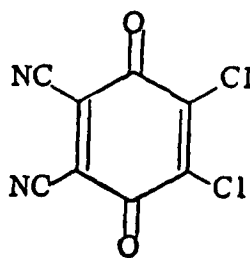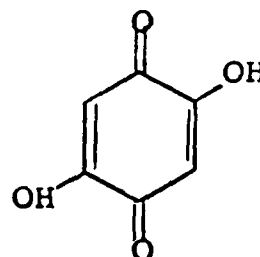TCNQ   fluoranil   chloranil

bromanil   DDQ   DHB

all reactions with molecular metallophthalocyanines yield insula-
tors, the structures of which no doubt consist of integrated
stacks (Figure 2C).[45,46] Doping experiments with the $[Si(Pc)O]_n$
polymers were thus carried out by stirring these materials
with solutions of the above quinones. The products were charac-
terized by elemental analysis and vibrational spectroscopy. As
can be seen in Table 3, large increases in electrical conductivity

Table 3. Electrical Conductivity Data for Polycrystalline Samples
of Molecular Phthalocyanines and Cofacial Phthalocyanine
Polymers with Various Dopants

Dopant[a]	Empirical Formula	$\sigma(\Omega^{-1} cm^{-1})300°K$	Activation Energy(eV)
none	$[Si(Pc)O]_n$	3×10^{-8}	
I	$\{[Si(Pc)O]I_{1.55}\}_n$	1.4	$0.04\pm.001$
Br	$\{[Si(Pc)O]Br_{1.00}\}_n$	6×10^{-2}	
K	$\{[Si(Pc)O]K_{1.0}\}_n$	2×10^{-5}	
DDQ	$\{[Si(Pc)O]DDQ_{1.00}\}_n$	2.1×10^{-2}	$0.08\pm.001$
DDQ	$\{[Si(Pc)O]DDQ_{0.35}\}_n$	6.2×10^{-2}	$0.05\pm.001$
TCNQ	$\{[Si(Pc)O]TCNQ_{0.50}\}_n$	2.8×10^{-3}	$0.09\pm.002$
ClA	$\{[Si(Pc)O]ClA_{0.14}\}_n$	1.8×10^{-3}	$0.11\pm.001$
Flr	$\{[Si(Pc)O]Flr_{0.23}\}_n$	7.2×10^{-4}	$0.13\pm.001$
Chl	$\{[Si(Pc)O]Chl_{.037}\}_n$	6.9×10^{-4}	$0.13\pm.002$
Brl	$\{[Si(Pc)O]Brl_{0.84}\}_n$	5.8×10^{-4}	$0.15\pm.001$
DHB	$\{[Si(Pc)O]DHB_{0.13}\}_n$	3.8×10^{-5}	$0.19\pm.005$
DDQ	$Ni(Pc)DDQ_{0.11}$	2.5×10^{-7}	0.43 ± 0.004
ClA	$Ni(Pc)ClA_{0.91}$	8.4×10^{-7}	$0.16^-0.002$

a
Flr = fluoranil; Chl = chloranil; Brl = bromanil; DDQ =
dichlorodicyanoquinone; ClA = chloranilic acid; DHB = dihydroxy-
benzoquinone.

accompany the quinone doping. Indeed, the DDQ-doped materials are as conductive as most of the halogenated polymers.[25,67] The temperature dependence of the conductivity of some representative samples is shown in Figure 6. The transport in these materials is thermally activated and least-squares fits to eq.(2) yield the activation parameters compiled in Table 3. There are some notable deviations from a linear ln σ vs. 1/T relationship (e.g., the ${[Si(Pc)O]TCNQ_{0.5}}_n$ sample shown in the Figure) and further investigations of the reasons for this behavior are in progress. Perhaps conduction is occurring through <u>both</u> $Pc^{+\delta}$ and $TCNQ^{-\delta}$ stacks with different temperature dependencies. Infrared
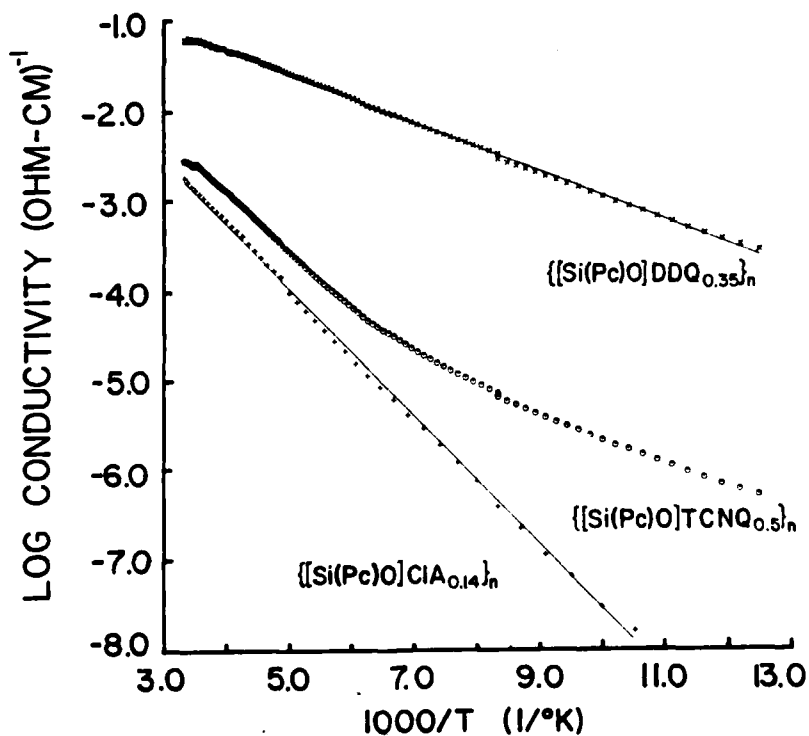

Fig. 6. Variable temperature powder conductivities of the siloxane phthalocyaninato cofacial polymer doped with high potential quinones. ClA = Chloranilic acid. From ref. 24.

spectral studies of the TCNQ-doped materials reveal a displacement of ν_{CN} to lower frequencies, consistent with electron density uptake by the quinodimethane.[68] Clearly oxidation of the $[Si(Pc)O]_n$ stack by high potential quinones occurs when a segregated stack structure is enforced. Moreover, this can result in facile charge transport.

In principle, it should also be possible to partially reduce phthalocyanines and to create conducting materials by injecting nonintegral amounts of electron density per site. A number of attempts have been made in this Laboratory to partially reduce metallophthalocyanines using alkali metals.[49] In all cases, the resulting materials were insulators, and it was suspected that nonstacked materials were being produced. A preliminary experiment was conducted in which $[Si(Pc)O]_n$ was reacted with potassium vapor in a sealed tube. The product was collected and handled at all times in an inert atmosphere. As can be seen in Table 3, a significant increase in electrical conductivity accompanies the potassium doping. Further efforts to refine the reductive doping procedure are now in progress.

CONCLUSIONS

Cofacial metallomacrocycle assembly methodology represents what is likely the most powerful approach yet devised for controlling molecular stacking relationships in low dimensional materials. In regard to fundamental understanding, we already have learned a great deal about bandwidth-conductivity and donor-acceptor relationships in conductive materials composed of molecular stacks. However, the surface has only been barely scratched in terms of the exciting research opportunities which await exploitation in this area. Further synthetic work offers the opportunity to make drastic changes in metallomacrocycle identity and electronic structure, stacking distance and bandwidth, interplanar relationships and phonon dynamics, and to correlate these chemical and structural modifications with physical observables. Already, new metal ions[69,70] and bridging functionalities[71,72] have been successfully introduced. Future studies with new types of dopants should provide much important information on donor-acceptor relationships and on those basic factors which stabilize the mixed valent state. A wide range of magnetic, charge transport, and optical experiments remain to be carried out. These experiments should ultimately provide invaluable information on how the chemistry and lattice architecture are connected to some of the fundamental characteristics of the molecular metallic state. Finally, studies of the processing characteristics of the $[M(Pc)O]_n$ materials are just beginning. Already we have learned that it is possible to produce films of $[Si(Pc)O]_n$ and that halogen doping results in substantial increases in electrical

conductivity.[72,73] Further efforts in this direction are under way.

ACKNOWLEDGMENTS

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